

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

A SERIES OF ALPHA HYDROXY ETHERS

by

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(A.B., Boston University, 1930)

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Master of Arts

1931

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Introduction

In the existing literature there was found no mention of the existence of ethers of the type formula $R-CHOH-O-C_2H_4OH$. There was, however, found mention of a compound, prepared by S.M. Losanitch, which was given the name acetaldehyde hydrate.¹ Losanitch states that the substance is prepared in considerable quantity during the passage of an electric current through a strong solution of acetaldehyde in water. The current must be of such a current density that twenty bubbles of carbon dioxide are given off per second. It was impossible to determine many of the physical properties of the liquid, since it was found to be very unstable. The liquid possessed the odor of acetaldehyde and the reactions characteristic of aldehydes in general. The substance was found to be neutral when freshly prepared, but on standing became acidic. From these considerations and a quantitative analysis, he considered the compound to possess the formula, $CH_3-CHOH-O-CHOH-CH_3$.

H. Adkins and his associates propose the theory that there exists in a solution of an aldehyde in an alcohol, an equilibrium between the alcohol, the aldehyde and a substance known as a hemi-acetal.² The formula of the acetal must be $R-CHOH-O-R'$. The existence of this equilibrium was shown by the study of refractive indices taken during the formation of acetals. Since such an equilibrium exists it would seem likely that any attempt to prepare the intended ethers might result in the formation of an aldehyde and an alcohol.

It was shown that a small amount of α -chloroether results from the chlorination of a large amount of ethyl ether.³ The

The first part of the report deals with the general situation of the country and the progress of the work. It is followed by a detailed account of the various projects and the results achieved. The report concludes with a summary of the work done and the prospects for the future.

The second part of the report deals with the financial aspects of the work. It gives a detailed account of the income and expenditure of the organization and shows how the funds have been used. It also gives a statement of the assets and liabilities of the organization.

The third part of the report deals with the administrative aspects of the work. It gives a detailed account of the organization of the work and the methods used to carry it out. It also gives a statement of the personnel of the organization and the work done by each of them.

The fourth part of the report deals with the social aspects of the work. It gives a detailed account of the social conditions of the country and the progress of the social work. It also gives a statement of the social work done by the organization and the results achieved.

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chloroether when treated with water at about 50°C . produced a liquid, which was given the formula $\text{CH}_3\text{-CHOH-O-C}_2\text{H}_5$. This compound was extremely unstable and could not be distilled. Even at the temperature of formation, there was a great tendency for the compound to dissociate into the alcohol and the aldehyde.

Due to the large amount of ethyl ether required to produce a reasonable amount of the mono chloro ethyl ether, it was not considered feasible to prepare the ether.

In summary, the purpose of these investigations is to prepare a series of α hydroxy substituted ethers, derivatives of ethylene glycol. The type formula of the series shows that the first member would be an isomer of glycerol, no isomer of which is yet recorded in the literature.

1. The first part of the paper discusses the importance of the study of the history of the United States. It is argued that a knowledge of the past is essential for a full understanding of the present and for the development of a sound policy for the future. The author points out that the United States has a long and rich history, and that it is one of the most powerful and influential nations in the world. It is therefore essential that we should have a clear understanding of our own history, and of the history of the world, in order to be able to make the most of our present and future opportunities.

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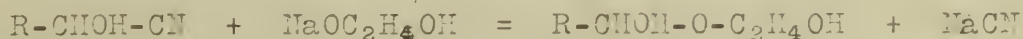
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Experimental

A. The Reaction of Cyanhydrins with Mono Sodium Glycollate

The method first attempted for the preparation of the ethers was based upon the Williamson synthesis. The cyanide derivative of the aldehyde was reacted with the mono sodium derivative of ethylene glycol.



I. The Preparation of Acetaldehyde Bisulfite

In order to prepare the cyanhydrin of the aldehyde it was thought more convenient to prepare first the aldehyde bisulfite addition product, which was carried out as follows:⁴

150 g. of sodium bisulfite was shaken with 200 cc. of water for about two hours, and then filtered. The resulting solution possessed a specific gravity of 1.35-40.

The acetaldehyde was prepared by distilling paraldehyde from benzene sulfonic acid. 100 g. of paraldehyde and 8 g. of benzene sulfonic acid were placed in a round bottom flask, fitted with an efficient fractionating column. The mixture was distilled from a water bath, and only that part of the distillate boiling under 30°C. was accepted as pure acetaldehyde.

The acetaldehyde and the sodium bisulfite solution were cooled to 0°C. and then the acetaldehyde was added slowly to the bisulfite solution, with frequent shaking. Considerable heat was liberated and it was necessary to keep the flask containing the mixture immersed in ice water. The quantities used

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were equimolecular with a ten percent excess of the aldehyde to compensate for that lost through evaporation. It was found that the solution formed was turbid, but that no crystals separated even after cooling to -15°C . The procedure was repeated with the same results. There was then obtained, by evaporation on a water bath, a white crystalline solid, extremely soluble in water and possessing the odor of acetaldehyde.

II. The Preparation of Acetaldehyde Cyanhydrin.

To prepare the cyanhydrin the bisulfite addition product was dissolved in the least amount of water and a saturated solution of an equivalent amount of potassium cyanide was added to the solution of the bisulfite. A small amount of heat was liberated, but no oil was observed to separate from the solution. The extraction of the cyanhydrin with ether was attempted but there was no residue upon evaporation of the ether extract. The most obvious explanation is that the cyanhydrin is too soluble in water to permit its separation. It was not possible for the writer to find methods for the preparation of the acetaldehyde cyanhydrin.

Other attempts were made to prepare the cyanhydrin of acetaldehyde. Gaseous hydrogen cyanide was passed into ether solutions of acetaldehyde. Acetic acid was added to ether solutions of the acetaldehyde, contained in a flask over sodium cyanide. Liberation of hydrogen cyanide took place but no large amount of acetaldehyde cyanhydrin was separated. Especially in the presence of water no cyanhydrin separated. Even when prepared the cyanhydrin was found to be unstable to ordinary conditions, and slowly turned red upon standing

1871

My dear Sir,

I have the honor to acknowledge the receipt of your letter of the 14th inst. in relation to the above named matter.

I am sorry to hear that you are not satisfied with the result of the investigation.

I have been very anxious to get the matter settled as soon as possible.

I have been very busy lately, and have not had time to attend to the matter as much as I would like.

I am sure that you will understand my position.

I am, Sir, very respectfully,
Your obedient servant,
J. H. [Name]

I am, Sir, very respectfully,
Your obedient servant,
J. H. [Name]

at room temperature. The amounts prepared were too small to be of use in synthesis of the ethers.

III. The Reaction of Acetone Cyanhydrin and Sodium Glycollate

The cyanhydrin of acetone was prepared by the addition of saturated potassium cyanide to a paste of acetone sodium bisulfite in water. Neither the bisulfite compound nor the cyanhydrin were appreciably soluble in water and were thus easily separated from water. The method of preparation was the same as that attempted in the case of the acetaldehyde. The cyanhydrin was found to turn color so readily upon the application of heat that it was not considered advisable to distill the cyanide. The only method of purification was drying with potassium carbonate for two hours.

III. a. The Preparation of Mono Sodium Glycollate.

A British patent describing the preparation of mono sodium glycollate was followed⁵. According to this method molecular quantities of ethylene glycol were dissolved in a 33% solution of equimolecular quantity of sodium hydroxide. The water was driven off by heating under reduced pressure and then the last traces were removed by heating the solid to the boiling point in a small stream of hydrogen. The preceding method was found to be less satisfactory, from the point of view of the time used, than the following method.

23 g. of sodium was dissolved in 62 g. of ethylene glycol, the addition taking place in small portions, and using a 5% excess of the ethylene glycol. The addition of the sodium took

place while the ethylene glycol was kept boiling. In this way less time was consumed during the reaction, due to the sodium being kept in the liquid state and to the addition product, or rather the substitution product, being kept dissolved in the ethylene glycol present. The excess of the glycol was removed by distillation in a small stream of hydrogen. The last traces of the glycol were removed by heating the solid to its boiling point over a free flame in an atmosphere of hydrogen. The glycollate when pure is in the form of small white crystals. It is very hygroscopic and readily takes up water, turning brown in the process. It can be preserved for an indefinite period, if it is kept out of the presence of air and moisture.

III b. The Reaction of the Cyanhydrin and the Glycollate

45 g. of the mono sodium glycollate was added to a 3-neck round bottom flask, of 500 cc. capacity. The flask was fitted with a mechanical stirrer, a condenser and a dropping funnel. To the glycollate was added a mixture of 45 g. of acetone cyanhydrin in 100 cc. of dry benzene. Benzene was found to be more efficient as a solvent for the cyanhydrin than any other liquid, except water. It was considered essential that the reaction mixture be dry in order that the product should not be decomposed by the action of the water. The acetone cyanhydrin was of an uncertain purity, due to the above properties of the compound, which prevented its purification. This fact made it necessary to use a 4 g. excess of the cyanhydrin.

The mixture was refluxed with constant stirring for four hours and then allowed to stand overnight. After this time the mixture had become darkly colored and a large amount of dark

The first of the three main divisions of the world is the
land. The land is divided into three parts: the
continent, the island, and the peninsula. The
continent is the largest part of the land, and it is
the part of the land which is not surrounded by water on
all sides. The island is a piece of land which is
surrounded by water on all sides. The peninsula is a
piece of land which is surrounded by water on three
sides. The second of the three main divisions of the
world is the water. The water is divided into three
parts: the ocean, the sea, and the lake. The ocean is
the largest part of the water, and it is the part of
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surrounded by land on all sides. The lake is a
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sides. The third of the three main divisions of the
world is the air. The air is divided into three
parts: the atmosphere, the stratosphere, and the
mesosphere. The atmosphere is the largest part of the
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oil was found at the bottom of the flask. This oil was mixed with a considerable amount of precipitated salt, in the bottom of the flask, to form a pasty mass. The solid was removed by filtration through glass wool, and was found to consist almost entirely of sodium cyanide. A water solution of the salt was not appreciably basic, indicating that the sodium glycolate had largely reacted. The benzene layer was separated and dried over potassium carbonate. It was then distilled from a water bath, and about 80 cc. of liquid was obtained below the boiling point of the benzene. This liquid was fractionated and the following fractions obtained:

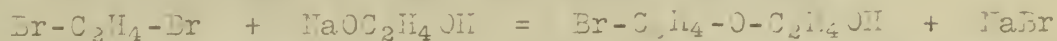
a. 55- 65°C. b. 65- 75°C. c. 75- 80°C.

The odor of each fraction was that of benzene. The fraction a) was found to react with benzaldehyde to form dibenzalacetone, indicating that the first fraction of about 60 cc. consisted almost entirely of acetone. The other fractions were mixtures of benzene and acetone. The dark reddish oil found at the bottom of the flask was considered to be a colored polymer of the cyanhydrin with the largest portion ethylene glycol.

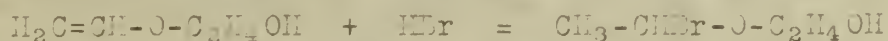
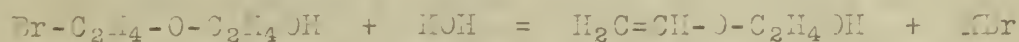
The results of the foregoing experiment showed conclusively that it was not worthwhile to continue further with attempts to prepare the ethers from the cyanhydrins. The explanation of the separation of the acetone in the reaction mixture may be that the cyanhydrin breaks up most easily into the acetone and hydrogen cyanide, or that the ether, which may have been formed, decomposes into the acetone and alcohol. The conclusive result is that, somehow, under the conditions of the experiment, the original carbonyl compound is regenerated.

B. Dihalogen Compounds with Mono Sodium Glycollate

This second method of attack was suggested by the possibility that ethylene bromide, as an example of the dihalogen compounds, might react with the mono sodium derivative of ethylene glycol according to the following reaction:



The diethylene bromohydrin, if prepared, should react ^{with} alcoholic potassium hydroxide, or a similar reagent, and split off hydrogen bromide. The resulting unsaturated compound should add hydrogen bromide and then be hydrolyzed as indicated by the following equations.



I. Ethylene Chlorobromide and Mono Sodium Glycollate

The above reaction between ethylene dibromide and sodium glycollate was attempted without satisfactory results. It was considered that the reaction might be completed more satisfactorily, if the two halogen atoms attached to the original halide were different. This difference in the halogen atoms, if one were bromine and the other chlorine, would certainly cause a substitution of one halogen rather than the other. It can readily be seen that if both halogens reacted with the sodium glycollate that the triethylene compound would be formed as indicated by the following equation.



On the other hand if only the bromine atom were substituted, as a study of the relative electronegativities would predict, the diethylene compound only would be formed, which should be diethylene chlorohydrin.

From the above reasoning it was decided to use ethylene chlorobromide in the reaction, in place of the ethylene dibromide. The reaction was carried out in the same manner as that in which the ethylene dibromide was used. The description of the procedure used in both reactions follows.

Equivalent quantities of the two components were used. 67 g. of ethylene chlorobromide was dissolved in 50 cc. of dry benzene and added to 25 g. of finely powdered sodium glycolate in a 500 cc. three neck, round-bottom flask. The flask was fitted with a mechanical stirrer and an efficient reflux condenser. The stirrer was started at such a rate as to keep the solid in suspension during the process, and the whole was warmed on a water bath for six hours. At the end of that time a positive test for the bromide ion was obtained. The mixture was allowed to stand over night and then the benzene layer was decanted. The solid in the bottom of the flask had formed into a glue like mass. This solid was then subjected to an analysis in order to roughly determine the amounts of sodium bromide and chloride present.

There was found to be about 70% of the theoretical amount of sodium bromide present in the mass. The determination of the sodium chloride showed about 5% of the theoretical amount of sodium chloride present. The water solution of the solid was not appreciably basic, indicating that most of the sodium glycolate had reacted.

From the values of the sodium bromide percentage in the solid it was calculated that there should be approximately twenty grams of the diethylene chlorohydrin in the benzene

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solution. When the benzene solution was subjected to distillation, after having been dried over potassium carbonate, there was found no liquid other than the benzene and a little of the unreacted ethylene chlorobromide. A very small amount of a dark colored oil was left in the flask, which did not amount to more than 2-3 cc.

The above experiments were performed twice with the ethylene dibromide, and in each case it was impossible to find any of the desired ethylene oxide chlorohydrin or bromohydrin. No satisfactory explanation of the phenomenon has yet been discovered.

II. A Reaction between Ethylidene Dihalides and Sodium Glycollate

Another modification of the Williamson synthesis for the preparation of the desired ethers is the reaction between the ethylidene halides and the mono sodium glycollate. This reaction was to have been tried, but upon recourse to the literature, mention was found of the preparation of the α chloroethers and of their properties. This article was briefly referred to in the introduction to this paper. Paul Fritsch found that the α chloro ethyl ether could be prepared by the direct chlorination of ethyl ether. The chloro ether upon treatment with water at 50°C. hydrolyzed to the hydroxy ether. The evidence given by this reaction is that the chloroether must hold the chlorine atom so loosely that it is extremely reactive. Indeed the halogen must be much more reactive and thus more readily substituted than either of the halogen atoms attached to the carbon atom of the ethylidene halides.

The most logical conclusion to the above argument is that, under the conditions of the experiment in which sodium glycolate

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 system of many parts, and it is not
 possible to describe it in a few words.

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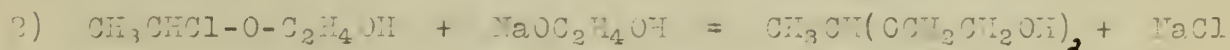
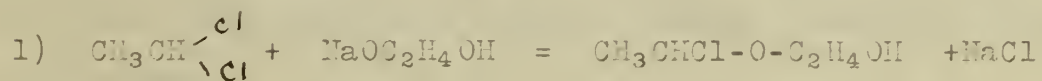
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is reacted with the ethylidene dihalides, that the second halogen atom of the ethylidene compound would be more readily substituted than the first. The product of the reaction would without doubt be the acetal of the ethylene glycol molecules with ~~acet~~aldehyde. The steps in the reaction are indicated by the following equations.



Reaction 2) would prevent the formation of any of the desired ether.

C. The Reduction of Ethyl Formate

It is known that aldehydes can be reduced by the action of finely divided nickel, when a mixture of hydrogen with the vapors of the aldehyde are passed over the finely divided nickel at a temperature near the boiling point of the alcohol, to which the aldehyde is to be reduced. It is customary to impregnate some material, such as pumice, with the finely divided nickel.

Inasmuch as it is possible to reduce the aldehydes, it seemed reasonable to suppose that ethyl formate could be reduced in the same manner, by virtue of its aldehydic group. This process, if successful, should produce a methyl ethyl ether, in which one of the hydrogens of the methyl group is substituted by a hydroxyl group. Several attempts were made to prepare this ether, as shown by the following experiments.

I. Preparation of a Nickel Catalyst (from the carbonate) ⁶

The catalyst for the reduction was prepared in the following manner. Infusorial earth was digested with enough concentrated nitric acid to give the mass the consistency of porridge. The process of digestion was continued for twenty-four hours on a water bath. The product was then diluted with its own volume of distilled water and filtered by suction. The precipitate was repeatedly washed until the filtrate showed only a faint reaction to litmus. The solid was thoroughly dried in an oven and stored in a tightly stoppered bottle for later use.

THE HISTORY OF THE CITY OF BOSTON

From its first settlement in 1630 to the present time. By
JOSEPH NEALE, Esq. of the Middle Temple, Barrister at Law.
In two Volumes. The first Volume contains the History from
1630 to 1780. The second Volume contains the History from
1780 to the present time. With a Plan of the City, and a
List of the Mayors, from 1630 to 1780. Printed by
J. NEALE, at the Sign of the Anchor, in Pall Mall.
1780.

The History of the City of Boston, from its first settlement in 1630 to the present time, is a subject of great interest and importance. It is a subject which has attracted the attention of many of the most distinguished writers of the age. The history of the city is a history of the growth of a great metropolis, and of the development of a great commercial empire. It is a history which is full of interest and of instruction. It is a history which is full of the most interesting and important events of the age. It is a history which is full of the most interesting and important characters of the age. It is a history which is full of the most interesting and important events of the age. It is a history which is full of the most interesting and important characters of the age.

100 g. of the earth was treated with 100g. of nickel nitrate dissolved in 175 cc. of water and the mass well stirred. It was warmed to 75°C . and poured into a solution of 44 g. of anhydrous sodium carbonate dissolved in 175 cc. of water. This was done slowly and with efficient stirring in order that the earth should hold the precipitated nickel carbonate as uniformly as possible. A small amount of carbon dioxide was liberated while the last of the nitrate was being added to the sodium carbonate. The product was filtered by suction and washed with four 75 cc. portions of distilled water. The catalyst was then removed from the filter and dispersed in 300 cc. of water. The product was washed, dried and then kept in an electric oven at 110°C . for eight hours.

To reduce the catalyst it was placed in a hard glass^{tube} about 2-3 feet in length. The tube was placed in an electrically heated combustion furnace. The ends of the tube were closed by rubber stoppers, each carrying a 450°C . thermometer and small glass tubing for the inlet and the outlet of the hydrogen. The thermometers were forced as far as possible into the body of the catalyst, which was packed very loosely in the tube. The tube and its contents were heated to a temperature of about 300°C . The hydrogen was passed through the tube at a rate of 3 bubbles per second. The time of the reduction occupied nearly six hours and was then not considered to be entirely complete. The method for the preparation of the catalyst was adapted from the reference noted.

The first part of the report deals with the general situation of the country. It is a very interesting and informative study of the country's development. The author has done a great deal of research and has gathered a wealth of material. The report is well written and is easy to read. It is a valuable contribution to the study of the country's development.

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II. The Catalytic Reduction of the Ethyl Formate

The method used for mixing the hydrogen gas with the correct proportion of the ethyl formate was to bubble the hydrogen through ethyl formate in a gas absorption bottle. The temperature of the ethyl formate was kept at about 40°C. to insure the passage of enough ethyl formate through the tube with the hydrogen. The vapors issuing from the farther end of the reaction tube were passed into a series of two 8 in. test tubes, immersed in an ice bath, where they were condensed. After a period of eight hours only 10 cc. of liquid was condensed.

The procedure was evidently not very valuable. The ethyl formate was the only constituent of the condensed vapors, showing that reduction either had not taken place or that the product formed was a gas at the temperature of the ice bath. There were no traces of compounds containing hydroxyl groups since the compound was not reactive with acetyl chloride. The gas which issued from the end of the reaction tube possessed a pyridine-like odor. The experiment was repeated with a new charge of the catalyst, using the same conditions and the results obtained were similar.

III. The Preparation of a Nickel Catalyst (from the nitrate)

It was considered possible that the catalyst used in the above described experiment was not suitable for that type of reduction, since, according to the literature, the catalyst had been prepared mainly for the purpose of liquid hydrogenation under pressure. Therefore a catalyst was prepared according to the method of Sabatier and Senderens.⁷

A suspension was made of 25 g. of asbestos in 400 cc. of a 10% solution of nickel nitrate. The asbestos was of commercial grade, acid washed and shredded. The mixture was allowed to stand for twenty-four hours and then sucked dry on a filter paper. The asbestos was heated over a small flame in a large evaporating dish, in order that the asbestos might be well spread out during the heating. The heating was continued until no more nitrogen dioxide was given off, and the asbestos had become dark gray in color. The reduction of the catalyst was carried out in the same manner as that used during the reduction previously described. The temperature was this time raised to 350°C . during the passage of the hydrogen. The reduction was considered complete when the water generated by the reaction no longer came over. The time of the reduction was cut down to two hours with the catalyst prepared in this manner, and the asbestos was much more metallic than that prepared from the carbonate.

IV. The Reduction Of Ethyl Formate (Catalyst from Nickel Nitrate)

The ethyl formate was again passed through the tube, being previously mixed with hydrogen gas. The method of introduction of the ester was this time slightly different from that employed in the previous reduction. In the two hole rubber stopper which closed the inlet end of the catalytic tube was the thermometer and also a Y tube. To one arm of the Y tube was attached a rubber tube which ran to the hydrogen tank. To the other arm of the tube attached a glass tube, leading to a reservoir from

The first part of the paper discusses the importance of the study of the history of the United States. It is argued that a knowledge of the past is essential for a full understanding of the present. The author then goes on to discuss the various factors that have shaped the development of the United States, including the role of the government, the influence of the economy, and the impact of the culture. The paper concludes by suggesting that a study of the history of the United States is not only a valuable academic exercise, but also a necessary one for anyone who wishes to understand the world in which we live.

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which ethyl formate ran slowly down the tube, through the Y tube and into the end of the catalytic tube. The catalytic tube was kept at a temperature of 150°C . so that the ethyl formate upon coming into contact with the tube vaporized and passed with the hydrogen through the tube. The rate of addition of the ethyl formate to the tube was about a drop per second. The rate of hydrogen was about twenty bubbles per second. There was 15 cc. of liquid collected in the test tubes, previously described, after about an hour of operation. The distillate was tested and found to contain only ethyl formate with a small amount of ethyl alcohol and formic acid. These experiments give rather conclusive evidence that ethyl formate cannot be reduced in this manner to the hydroxy ether.

V. The Reduction of Ethyl Formate with Sodium Amalgam in Alcohol

Aldehydes have also been reduced through the action of sodium amalgam upon either water or alcohol, the hydrogen being liberated in the nascent state.

Since the product of the reduction of ethyl formate would be likely to be unstable in the presence of water, it must be prepared by the reaction of sodium amalgam upon absolute alcohol, if it can be prepared in this manner.

37 g. of ethyl formate was dissolved in 150 cc. of absolute alcohol in a 200 cc. side arm filter flask. An amalgam of 23 g. of sodium in 500 g. of mercury was added to the alcohol in small pieces. The mixture was allowed to stand overnight and in the morning a large part of the sodium had re-

acted with the alcohol. the reaction was completed by refluxing the mixture on a water bath for six hours. At the end of this time there was no hydrogen liberated and the mercury had become entirely mobile. The reaction mixture was distilled under atmospheric pressure and the only liquid found in the distillate was ethyl alcohol. The explanation is either that the ethyl formate may have been reduced to a compound having a boiling point very close to that of the ethyl alcohol, or that the ethyl formate may not have been reduced. In the latter case the ethyl formate may have evaporated during the process.

VI. The Reduction of Ethyl Formate with Sodium Amalgam in Butyl Alcohol

The above noted possibility, that the reduction product of the ethyl formate may have been so close to the ethyl alcohol in respect to their boiling points that the two could not be separated, led to the use of butyl alcohol in the place of the ethyl alcohol.

The procedure was the same in most respects as that used in the case of the ethyl alcohol. The main difference was that the ethyl alcohol required a much less period of reaction than did the butyl alcohol. The butyl alcohol was heated for two days on a water bath before the reaction was complete. The distillation of the mixture yielded in this case also nothing but the excess of the alcohol in which the ethyl formate was dissolved. The most obvious explanation is that the ethyl formate was not reduced by either of these methods, and was lost through evaporation during the heating.

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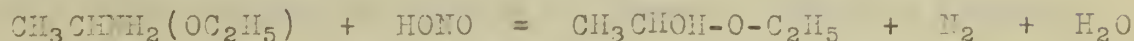
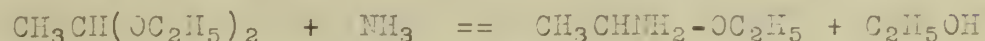
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D. The Use of Diethyl Acetal as a Starting Point

Another attempt was made to prepare the ethers by treating acetal in two different ways.

I. The Treatment of Acetal with Ammonia.

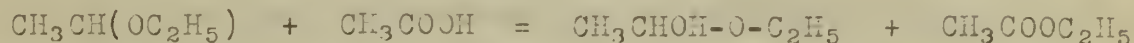
The reaction was expected to take place according to the following equations.



The reaction was attempted in the manner of ammonolysis of esters. One equivalent weight of concentrated ammonia water was allowed to stand with an equivalent weight of acetal. After several weeks of standing the two layers had not disappeared, giving evidence that no reaction had taken place.

II. The Reaction of Acetal with Acetic Acid.

The second experiment with the acetal as a starting point is given in the following equation:

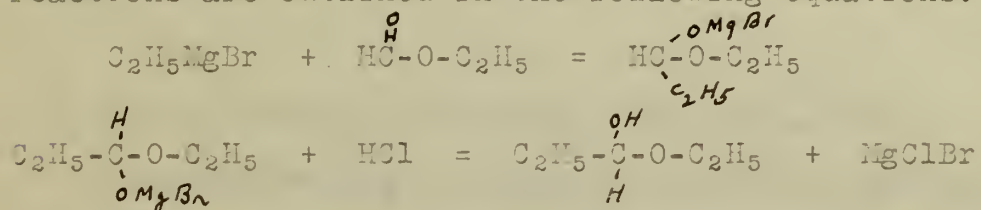


The procedure follows. 32 g. of acetal was mixed with 15 g. of glacial acetic acid and the mixture was refluxed for three hours. At the end of that time no reaction had taken place. The distillation of the reaction mixture yielded nothing but acetic acid and acetal.

It appears from the above experiments that acetal is not a suitable starting point for the preparation of the ethers.

E. The Reaction of Ethyl Formate with Ethyl Magnesium Bromide

Carbonyl compounds are known to react with the alkyl magnesium halides, adding to the carbon-oxygen double bond giving a compound which hydrolyzes with any hydroxyl containing compound to an alcohol. Inasmuch as ethyl formate contains a carbonyl group in the linkage characteristic of aldehydes, it was considered that ethyl formate might react with the ethyl magnesium bromide to give an addition product, wherein the double bond was broken. The resulting compound if treated with dry HCl should form an α -hydroxy ether. The reactions are outlined in the following equations.



The reaction was carried out in the following manner:

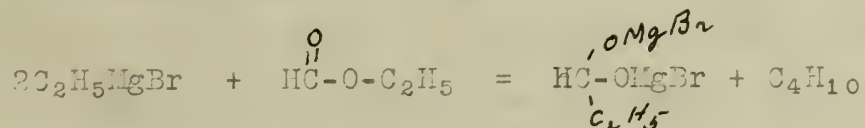
I. Preparation of the Grignard Addition Product

To 6.1 g. of magnesium turnings, covered by 100 cc. of dry ether, was added 27 g. of dry ethyl bromide, dissolved in 50 cc. of dry ether. The ethyl ^{bromide} ~~formate~~ was added drop by drop to the magnesium, at a rate sufficient to keep the ether boiling gently. The reaction mixture was contained in a 500 cc. three neck flask, fitted with a mechanical stirrer, an efficient reflux condenser and a separatory funnel. The bromide was added over the course of an hour.

After the reaction was complete the ethyl magnesium bromide in ether solution was siphoned over into a 500 cc. three neck flask. The siphon was arranged with a stop cock in the cir-

The first part of the paper discusses the importance of the study of the history of the United States. It is argued that a knowledge of the past is essential for a full understanding of the present. The author then proceeds to a detailed examination of the early years of the Republic, from the time of the signing of the Declaration of Independence to the end of the War of 1812. This section covers the political, social, and economic developments of the period, and the role of the various states in the formation of the new nation. The author also discusses the influence of foreign powers on the young United States, and the challenges faced by the government in its early years. The second part of the paper is devoted to a study of the literature of the period, and the role of the writers in shaping the national identity. The author examines the works of such writers as Washington Irving, James Fenimore Cooper, and Henry David Thoreau, and discusses the ways in which their writing reflected the values and beliefs of the time. The paper concludes with a discussion of the legacy of the early years of the Republic, and the lessons that can be learned from the experience.

cuit so that the ether solution could be allowed to drop slowly into the flask. The receiving flask was immersed in an ice bath, and contained a solution of dry ethyl formate, 37 g. in 100 cc. of ether. The amount of ethyl formate used was twice the equivalent amount in order that the following reaction might not take place.



There was a violent reaction with the addition of each drop of the grignard reagent. The temperature was kept low, below 10°C.

II. The Acidulation of the Addition Product

In this process the additon product of the ethyl formate and the ethyl magnesium bromide was treated with dry hydrogen chloride. The method was as follows:

The hydrogen chloride was generated in a liter flask, fitted with a dropping funnel and an outlet tube. The latter was connected with an empty wash bottle and this to a Woulff bottle with a safety ^{tube} ~~bottle~~, containing concentrated sulfuric acid. The latter bottle was connected in turn with another bottle containing concentrated sulfuric acid. From there the gas was led through an empty wash bottle, in order to absorb any sulfuric acid, and then into the addition product dissolved in ether.

The reaction flask was the same as that used in the previous reaction. The three necks were provided with (1) an inlet tube for the gas leading nearly to the bottom of the flask, (2) a thermometer, (3) an outlet tube for the gas, which leads to

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2. The second part of the document is a letter from the Secretary of the War Department to the Secretary of the Treasury, dated January 10, 1862. The letter is addressed to the Secretary of the Treasury, and is signed by G. K. Warren.

3. The third part of the document is a letter from the Secretary of the War Department to the Secretary of the Treasury, dated January 10, 1862. The letter is addressed to the Secretary of the Treasury, and is signed by G. K. Warren.

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a bottle, partly filled with 10% sodium hydroxide, above which the outlet tube is adjusted. The sodium hydroxide bottle was connected with an aspirator through which water was slowly running. There was a calcium drying tube between the sodium hydroxide bottle and the reaction flask.

During the reaction the contents of the flask were kept below 5°C. by immersion in the ice-salt bath. The hydrogen chloride was passed in as rapidly as the temperature would allow. It was noticed that during the reaction that two layers separated and that the lower layer was reddish-brown in color. When the hydrogen chloride caused no further rise in temperature the stream of the gas was discontinued and the ~~the~~ two layers separated. The lower layer was found to be very viscous, in fact the viscosity was so great that there was difficulty in running the lower layer through the separatory funnel.

The reaction was repeated with twice the previous quantities in order to obtain larger quantities of the unexpected lower layer. The reaction proceeded in the same way and gave the same results. The amount of the lower layer was in the first reaction about 50 cc. and in the second was about 125 cc.

The properties of the lower are as follows.

III. Analysis of the Reaction Product

The physical properties were

1. High viscosity
2. Aldehyde odor
3. Darkness of color, increasing with standing.

The chemical properties were as follows:

1. The substance was found to be very reactive with water giving a yellowish colored liquid, soluble in ether. The latter fact was most unusual at first sight. The explanation arrived at was that the lower layer dissolved the magnesium bromochloride, producing the salting out effect. The remarkable part is that the magnesium halide should be so soluble in the liquid that it entirely dissolved.

2. The layer produced by the treatment with water was dried over sodium sulfate and ~~treated~~^{reacted} as follows:

a. Negative reaction with Fehlings solution showing the lack of any aldehyde.

b. Considering that the aldehyde if formed, might have polymerized, the liquid was boiled with dilute sulfuric acid and distilled. The distillate gave no test with Fehlings solution.

c. The liquid gave the characteristic color with Schiff's reagent, i.e. the reddish-blue color produced with aldehydes.

d. The liquid possessed no definite boiling point. Upon distillation of the liquid there was obtained a small amount of ethyl bromide (possibly unreacted ethyl bromide).

e. There was also obtained a test for ethyl alcohol by forming the 3,5 dinitrobenzoic ester of ethyl alcohol from the distillate above.

3. A portion of the undecomposed acidulation product was distilled from a water bath and the distillate was found to contain some ethyl alcohol, confirmed by the derivative used in the previous paragraph. There was also found

some ethyl bromide and ether.

- a. A test was made for acetaldehyde with 2,4 dinitro phenylhydrazine but no derivative was found to be formed.

The exact nature of the lower layer formed during the reaction is still a mystery. There was certainly some ethyl bromide, ethyl alcohol and ether in the layer. The other substances present may very well be complex and unstable. The dark color at the time of formation leads one to think that such is the case, since the substance or substances present would not be expected to be colored in that manner. unless extensive polymerization had taken place.

It seems to the writer that further work might well be done on the determination of the nature of the compounds formed in the reaction. It is regretted that he did not have time to continue the work.

F. Summary.

The object of the present research problem has been to prepare the dihydroxy ethers, characterized by the type formula, $R-CHOH-O-CH_2CH_2OH$.

In pursuit of this ether several methods have been tried. The reaction between cyanhydrins and the mono sodium derivative of ethylene glycol has been studied. The reaction studied in detail was that between mono sodium glycollate and acetone cyanhydrin. It was shown by this example that such a reaction is not capable of producing the aforementioned ethers. The products of the reaction were acetone and hydrogen cyanide, which reacted with the sodium glycollate to give sodium cyanide and ethylene glycol. Thus it is shown that the cyanhydrins have too great a tendency to break up into hydrogen cyanide and the original aldehyde or ketone..

A second attempt was made to prepare the ethers through the medium of a compound ~~of~~, $CH_3CHCl-O-CH_2CH_2OH$. Several attempts were made to prepare this compound by the interaction of sodium glycollate and ethylene dibromide, and later with ethylene chlorobromide. These attempts failed for some unapparent reason.

Other attempts were made to prepare $CH_2OH-O-CH_2CH_3$ by the reduction of ethyl formate. It was found impossible to reduce the ester either with hydrogen in the presence of a nickel catalyst or with sodium amalgam in ethyl alcohol and in butyl alcohol.

Attempts were made to treat acetal with ammonia and with acetic acid in order to prepare in the first case the amino ether, from which the hydroxy ether could be prepared by the treatment with nitrous acid, and in the second place to prepare the hydroxy ether directly.

Another method of approach to the subject was by the acidulation of the addition product of ethyl formate and ethyl magnesium bromide. A liquid was obtained which was found to contain ethyl bromide, ethyl alcohol and some ether. Other substances might easily have been present, but none were identified. It could not be determined whether or not the ether was present, especially as the ether would be expected to be very unstable.

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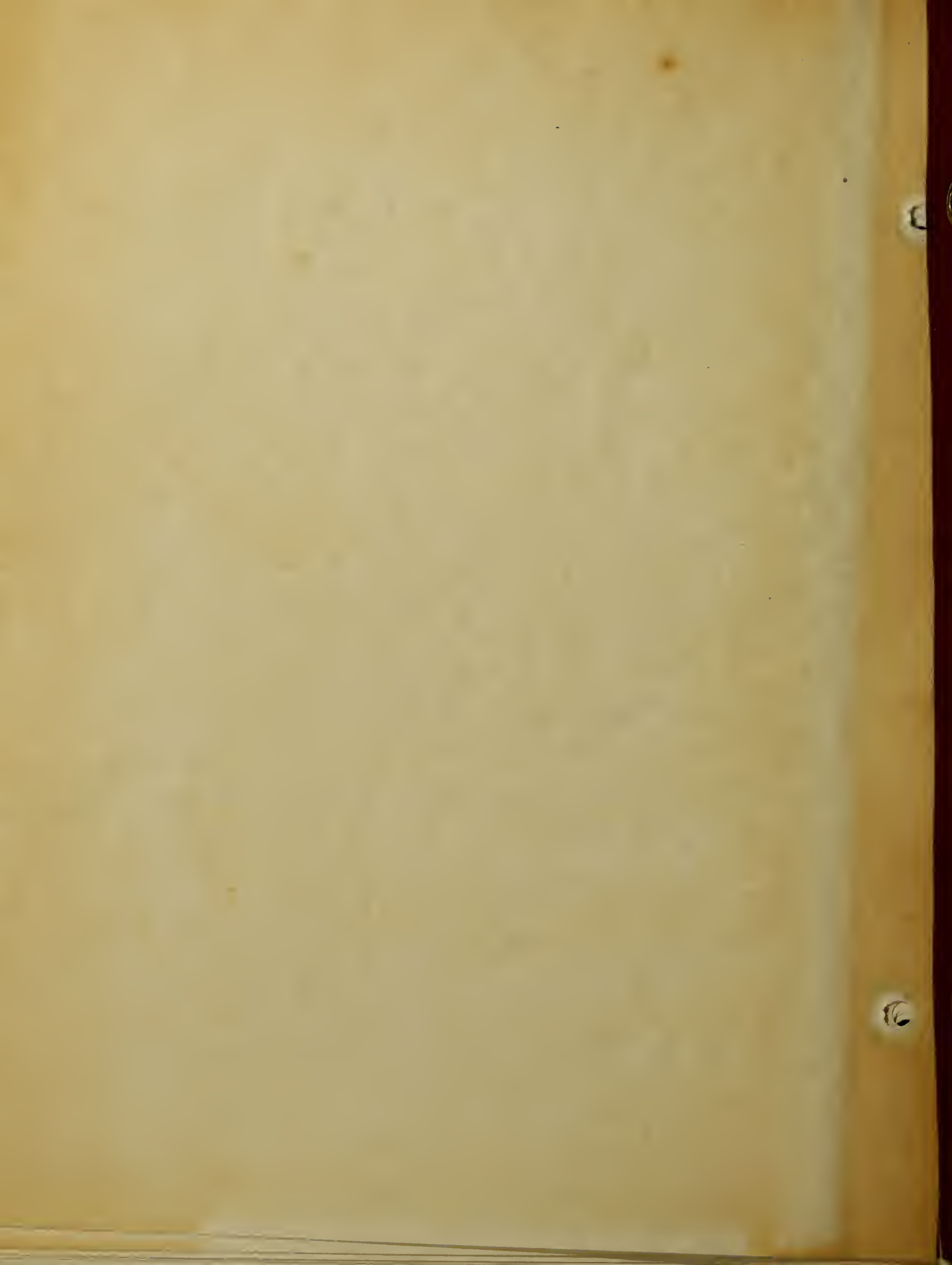
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